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(21) International Application Number: PCT/US90/01837 (22) International Filing Date: 9 April 1990 (09.04.90) (30) Priority data: 347,647 5 May 1989 (05.05.89) US (71) Applicant: GAF CHEMICALS CORPORATION [US/ US]; 1361 Alps Road, Wayne, NJ 07470 (US). (72) Inventor: PLOTKIN, Jeffrey, S. ; 7 Carpenter Ct., Monsey, NY 10952 (US). (74) Agents: MAUE, Marilyn, J. et al.; GAF Corporation, Pa- tent Dept., Building No. 10, 1361 Alps Road, Wayne, NJ 07470 (US).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (Eu- ropean patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European pa- tent), SE (European patent). Published <i>With international search report.</i>
(54) Title: PRODUCTION OF LACTONES FROM DIOLS (57) Abstract A method for converting 1,4 and 1,5 aliphatic saturated diols to lactones is disclosed wherein the diol is reacted with a chemical oxidizing agent and a ruthenium containing catalyst at temperatures substantially less than 200°C. The reaction proceeds quickly and produces high yields of the desired product.		

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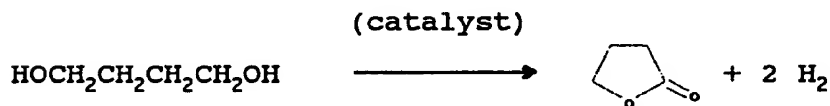
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PRODUCTION OF LACTONES FROM DIOLSBACKGROUND OF THE INVENTIONI. Field of the Invention

This invention pertains to the field of conversion of diols to lactones by oxidation in the presence of a catalyst. More particularly, it relates to the improved production of lactones at low temperatures utilizing ruthenium containing catalysts.

II. Description of the Prior Art

It is known to convert diols to lactones by heating the diol in the presence of a copper chromite catalyst. See, for example, Ulmanns Encyclopedia of the Chemical Industry, Vol. A4, p. 495-498. The general reaction sequence using a butane-1,4-diol as the starting material, is as follows:

15 Reaction Sequence 1

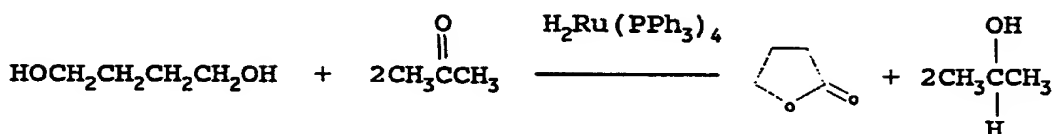
The major problem, however, with this reaction is that it requires excessively high temperatures, namely, temperatures in excess of 200°C. Consequently, if one is preparing a lactone which is thermally sensitive, the high temperature of preparation severely inhibits or renders impossible the carrying out of the dehydrogenation reaction since any product which is formed is destroyed.

It has also been reported that soluble, homogeneous ruthenium complexes can promote dehydrogenation

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of 1,4-diols if appropriate hydrogen acceptors are present.
S. Murahashi, et al., J. Org. Chem., 1987, 52, 4319.



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These reactions also require elevated temperatures, e.g., 120-200°C, in order to process at reasonable rates. Also, the catalysts are quite expensive.

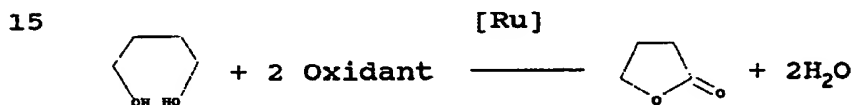
It is also known that ruthenium tetroxide is capable of acting as a stoichiometric oxidant for converting alcohols to ketones, aldehydes to acids and ethers to esters or lactones. It is further known that ruthenium can be used in catalytic amounts in the form of ruthenium trichloride or ruthenium oxide if used with an oxidant, such as, sodium hypochlorite to convert ethers to esters. (See "Metal-Catalyzed Oxidations of Organic Compounds" by R.A. Sheldon and J.K. Kochi, Academic Press (1981), Chapter 12.) Indirect electrooxidation of alcohols and diols to acids and lactones, respectively, has been reported using ruthenium-based catalyst system. This was accomplished by utilizing a double mediating system of $\text{RuO}_4/\text{RuO}_2$ and Cl^+/Cl^- redoxes in an aqueous-organic two-phase system. See J. Org. Chem., 1986, 51, p. 155-161.

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SUMMARY OF THE INVENTION

I have discovered a method for producing lactones from 1,4 and 1,5 saturated aliphatic diols which can be conducted at temperatures substantially less than 200°C. and which proceeds with relative rapidity and produces high yields of the desired product. More particularly, I have discovered that this can be accomplished by reacting the starting diol in the presence of a chemical oxidizing agent and a ruthenium containing catalyst. The reaction is carried out at a temperature below 100°C. The preferable temperature range for the reaction is from about -20° to 50°C. Preferably, the reaction is carried out at ambient temperatures. Thereafter, the lactone is recovered from the reaction mixture.

DESCRIPTION OF THE PREFERRED EMBODIMENT

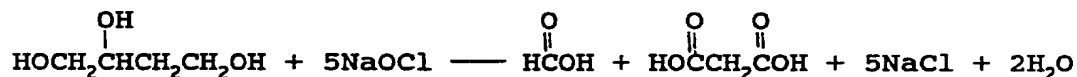
A variety of saturated aliphatic 1,4 and 1,5 diols can be utilized with the present invention. The diols may be substituted with functional groups which are resistant to oxidation, for example, esters, halogen, and cyano groups. Some examples are given in the table. As shown in the Table, 1,4-butane diol and 1,5-pentane diol were oxidized smoothly with high selectivity to the butyrolactone and valeralactone, respectively. 2-Methyl-1,4-butanediol was oxidized to two isomers, namely, 3-methyl butyrolactone and 4-methyl-butyrolactone. Dimethylolnorbornane was also cleanly oxidized in high yield to its corresponding lactone. Diethylene glycol

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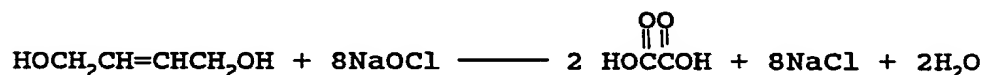
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cyclized much more slowly to dioxanone; other unidentified compounds were also found as shown by gas chromatography.

Certain functional groups do not respond desirably to the conditions required in the inventive process. Two examples are butanetriol and 1,4-butenediol. In the case of butanetriol, nearly five equivalents of NaOCl were taken up. It is known from the literature that vicinal glycols are cleaved to acids by ruthenium tetroxide. The reaction shown below can account for consumption of five equivalents of NaOCl.



Oxidation of 1,4-butenediol did not give dehydrobutyrolactone. Nearly seven equivalents of NaOCl were taken up. The following reaction accounts for eight equivalents of NaOCl.



The conditions for the above reactions are those set out in the footnote to the table hereinbelow.

Suitable oxidizing agents for use in the present invention include commonly available materials, such as, NaOCl, Ca(OCl)₂, t-butylhydroperoxide, methyl morpholine-n-oxide, sodium periodate, and hydrogen peroxide. NaOCl and Ca(OCl)₂ are preferred.

Suitable ruthenium catalysts which can be used are those commercially available and include ruthenium oxide, ruthenium on carbon, ruthenium on alumina, ruthenium trichloride, H₂Ru(PPh₃)₄, and Cl₂Ru(PPh₃)₄. However, essentially any ruthenium-containing material can be used

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so long as the oxidant can oxidize the ruthenium to the active form.

The process of the present invention may be carried out by dissolving the diol in a suitable solvent.

5 Solvents which may be used are those which are resistant to oxidation by the oxidizing agent. Typically, such solvents include water, ethyl acetate, acetonitrile, dimethylformamide, sulfolane, and the like. The preferred solvent is water since it is most readily available and
10 least expensive. A catalytic amount of the ruthenium compound is then added to the solution. The catalyst may or may not dissolve in the particular solvent used. If it does dissolve, this aids in the rapidity of the reaction. Alternatively, the catalyst may be added directly to the
15 diol without the presence of a solvent. The catalyst is dissolved in the diol and the oxidant is added directly to this mixture. The mixture is heated or cooled to the desired reaction temperature and the oxidant is added, usually in drop-wise fashion into the solution with
20 stirring. Usually, the mixture of the diol and catalyst is colored. As the oxidant is added, the mixture or reaction solution becomes clear yellow, but then returns to the original color. As the reaction nears completion, the new color persists for longer periods eventually remains,
25 indicating the completion of the reaction.

In this process, the amount of starting diol may vary depending on the total amount of product required. The oxidant appears to react stoichiometrically with the diol so that the total quantity of oxidant needed to
30 complete the reaction corresponds to the stoichiometric requirements. The amount of catalyst to be added is essentially a catalytically effective amount, preferably in the range of from about 0.001 to 2.0 weight % based on the weight of the diol. The initial concentration of the diol

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in the solvent is from about 1.0 to 75.0 weight %, based on the total weight of solvent and diol. Preferably, the concentration of the diol is from about 5.0 to 25%. After the completion of the reaction, the lactone obtained can be separated from the reaction mixture by conventional working up procedures, e.g., distillation, etc.

Example 1:

One gram of butane diol was dissolved in 15 cc. of water. Ten milligrams of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ is added to the solution. At ice bath temperatures, an aqueous solution of 5.25% NaOCl was slowly dripped into the diol solution with stirring. With each additional drop of NaOCl, the solution turned from black to yellow and then quickly back to black. As the reaction neared completion, the yellow color persisted for longer periods. When the color remained yellow for 0.5 hours, the reaction was finished. The amount of NaOCl required to maintain the yellow color corresponded closely to the calculated amount needed for one gram of butane diol. Gas chromatographic analysis shows that no butane diol remained and the only material present was butyrolactone.

This reaction was carried out at a temperature range from 10° to 15°C., and the butane diol was converted quantitatively to butyrolactone in a short period of time. On a weight basis, the butane diol to $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ is 100-fold excess, while on a molar basis, the amount of butane diol to active ruthenium is 231:1. If the reactions are conducted at a higher temperature, lower levels of ruthenium can be used and still maintain a reasonable rate of reaction.

The following table illustrates a number of diols which can be converted to lactones and the yields of

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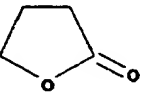

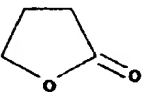

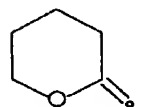
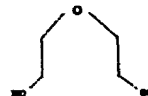
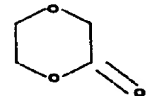
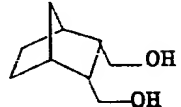
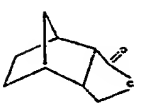
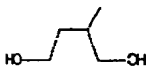
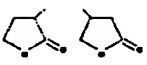

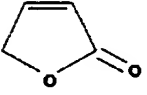
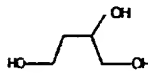
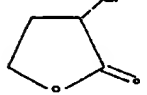
product obtained thereby. The selectivity of the process was followed by gas chromatographic analysis. In the table, the column entitled, "GC Selectivity" represents the percentage of the desired end-product achieved as shown on the gas chromatogram. Also illustrated in the table are the equivalents of NaOCl oxidant utilized. The gas chromatographic analysis was carried out using a DB-wax column 30 meters long with a diameter of 0.326 mm and a film thickness of 0.5 mm. The carrier gas was helium at the rate of 1 ml/min. The temperature program had an initial value of 125°C., and was increased at a rate of 4°C./ min. to a final value of 220°C. over a total of 100 minutes.

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TABLE

Oxidation of Diols to Lactones*

<u>Exp.</u>	<u>Diol</u>	<u>Desired Product</u>	<u>Conversion (%)</u>	<u>GC Selectivity</u>	<u>Equivalents of NaOCl</u>
1			100	100	2.05
2**			100	100	2.66
3			100	98	2.10
4			71	55	2.15
5			98.6	98	2.1
6			97	41, 59	3.2
7			100	0	6.84
8			100	0	4.76

* All reactions except exp. 2 were run with ten mg $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ as catalyst, 1 gram of diol in 15 cc H_2O . 5.25% aqueous NaOCl was used as oxidant. All reactions were run at 10-15° C.

** Catalyst was 0.2g 5% Ru/carbon.

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Example 2:

One milligram of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ was dissolved in ten grams of 1,4-butenediol. At ice bath temperature, 5.25% aqueous NaOCl was slowly added with stirring. After a
5 total of 550 ml, all 1,4-butenediol was consumed as detected by gas chromatography. The selectivity to butyrolactone was 80%; hydroxybutyraldehyde was also observed (10% selectivity). This example demonstrates that very low levels (.01 weight %) of catalyst can be used
10 although selectivity drops to 80%.

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CLAIMS:

1. A method for converting 1,4 and 1,5 aliphatic saturated diols to lactones comprising reacting the diol in the presence of an effective amount of a chemical oxidizing agent and a catalytic amount of a ruthenium containing catalyst at a temperature below 100°C and recovering the lactone produced.
2. The method of Claim 1 wherein the reaction is carried out at a temperature of from about -20°C to 100°C.
3. The method of Claim 1 wherein the reaction is carried out at ambient temperature.
4. The method of Claim 1 wherein the oxidizing agent is selected from the group consisting preferably of NaOCl, Ca(OCl)₂, t-butylhydroperoxide, methyl morpholine-n-oxide, sodium periodate, and hydrogen peroxide.
5. The method of Claim 1 wherein the catalyst is selected from the group consisting of ruthenium oxide, ruthenium on carbon, ruthenium on alumina, ruthenium tri-chloride, H₂Ru(PPh₃)₄, and Cl₂Ru(PPh₃)₄, wherein Ph is phenyl.
6. The method of Claim 1 wherein the amount of catalyst is in the range from about 0.001 to 2 weight percent based on the amount of the starting diol.
7. The method of Claim 1 wherein the concentration of starting diol is in the range from about 1 to 75%.

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8. The method of Claim 7 wherein the concentration of starting diol is from about 5 to 25%.

9. The method of Claim 1 wherein the catalyst is first dissolved in the starting diol in the absence of added solvent, and the oxidizing agent is added portionwise to the mixture until the reaction is completed.

10. The method of Claim 1 wherein the starting diol is first dissolved in a solvent which is resistant to oxidation, the catalyst is admixed to the resulting solution, the temperature of the mixture is adjusted to the desired temperature and the oxidizing agent is added portionwise to the mixture until the reaction is completed.

11. The method of Claim 10 wherein the solvent is selected from the group consisting of water, acetonitrile, dimethylformamide, and sulfolane.

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INTERNATIONAL SEARCH REPORT

International Application No **PCT/US90/01837**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC C07D 319/12 IPC (5): C07D 307/06; C07D 307/28; C07D 307/77; C07D309/04; C07D 309/12 U.S. CL: 549/295; 549/273; 549/274; 549/323; 549/299				
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁴</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">Classification System </td> <td style="width: 50%; border: none;">Classification Symbols</td> </tr> </table> <div style="margin-top: 10px;"> U.S. CL. 549/295; 549/273; 549/274; 549/323; 549/299 </div> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵</div>			Classification System	Classification Symbols
Classification System	Classification Symbols			
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴				
Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸		
Y	US, A, 4,465,847 (SHVO) 14 August 1984, col. 1-col. 4.	1-11		
Y	Journal of Organic Chemistry vol. 52(2), issued 1987, S. Murahashi et al., "Ruthenium-catalyzed oxidative transformations of alcohols and aldehydes to esters and lactones", See pgs 4319-4327.	1-11		
Y	R. A. Sheldon et al., "Metal-Catalyzed oxidations of Organic Compounds, "Chapter 12, Academic Press, New York, 1983. See pages 350-356.	1-11		
A	Journal of Organic Chemistry vol. 51(2); issued 1986, S. Torii et al., "Indirect electro oxidation of alcohols and aldehydes by using a double mediatory system consisting of RuO ₄ /RuO ₂ and Cl ⁺ redoxes in an aqueous-organic two-phase system", See pages 151-161.	1-11		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁵ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>				
IV. CERTIFICATION				
Date of the Actual Completion of the International Search ⁸ 05 JUNE 1990 International Searching Authority ¹ ISA/US	Date of Mailing of this International Search Report ⁹ <div style="text-align: center; font-size: 1.2em;"> 17 AUG 1990 </div> Signature of Authorized Officer ¹⁰ <div style="text-align: center;"> MARK W. RUSSELL </div>			